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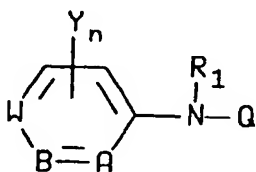
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(54) **N-arylhydrazine derivatives as insecticidal and acaricidal agents.**

(57) There are provided N-arylhydrazine derivatives of formula I



(I)

the use thereof for the control of insect and acarid pests and methods and compositions for the protection of crops from the damage and loss caused by said pests.

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BACKGROUND OF THE INVENTION

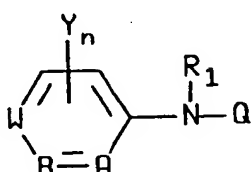
Certain insect and acarid pests are harmful and cause enormous losses annually in agricultural crops, stored products and human and animal health. It is an object of this invention to provide substituted N-arylhazirine derivatives which are effective agents for the control of pestiferous insects and acarina.

It is another object of this invention to provide a method for the protection of important agronomic crops from the harmful and damaging effects caused by insect and acarid pests.

It is a further object of this invention to provide insecticidal and acaricidal compositions.

SUMMARY OF THE INVENTION

The present invention provides a method for the control of insects or acarina which comprises contacting said insects or acarina or their food supply, breeding ground or habitat with an insecticidally effective amount of an N-arylhazirine derivative of formula I



(I)

wherein

A

is C-R₄ or N;

B

is C-R₅ or N;

W

is C-R₆ or N with the proviso that one of A, B or W must be other than N;

Y

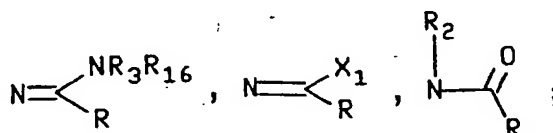
is hydrogen, halogen, CN, NO₂, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy or C₁-C₆ haloalkoxy;

n

is an integer of 0, 1 or 2;

Q

is



R

is hydrogen, C₁-C₁₀ alkyl optionally substituted with one or more halogens, C₃-C₆ cycloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, (C₁-C₄ alkyl)SO_x, (C₁-C₄ haloalkyl)SO_x, phenyl optionally substituted with one to three halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, (C₁-C₄ alkyl)SO_x, (C₁-C₄ haloalkyl)SO_x, NO₂ or CN groups, or phenoxy optionally substituted with one to three halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, (C₁-C₄ alkyl)SO_x, (C₁-C₄ haloalkyl)SO_x, NO₂ or CN groups,

C₃-C₁₂ cycloalkyl optionally substituted with one or more halogens, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, (C₁-C₄ alkyl)SO_x, (C₁-C₄ haloalkyl)SO_x, phenyl optionally substituted with one to three halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, NO₂ or CN groups, or phenoxy optionally substituted with one to three halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, NO₂ or CN groups, or

phenyl optionally substituted with one or more halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, NO₂ or CN groups; are each independently hydrogen or C₁-C₄ alkyl;

R₁ and R₂

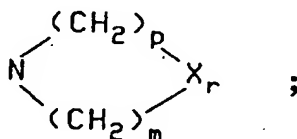
C₁-C₁₀alkyl optionally substituted with one or more halogen, hydroxy, C₁-C₄alkoxy, (C₁-C₄alkyl)SO_x, CONR₇R₈, CO₂R₉, R₁₀, R₁₁, C₃-C₆cycloalkyl optionally substituted with one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups, phenyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, CO₂ or CN groups, or pyridyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups,

C₃-C₁₀alkenyl optionally substituted with one or more halogen, hydroxy, C₁-C₄alkoxy, (C₁-C₄alkyl)SO_x, CONR₇R₈, CO₂R₉, R₁₀, R₁₁, C₃-C₆cycloalkyl optionally substituted with one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups, phenyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, CO₂ or CN groups, or pyridyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups,

C₃-C₁₀alkynyl optionally substituted with one or more halogen, hydroxy, C₁-C₄alkoxy, (C₁-C₄alkyl)SO_x, CONR₇R₈, CO₂R₉, R₁₀, R₁₁, C₃-C₆cycloalkyl optionally substituted with one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups, phenyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, CO₂ or CN groups, or pyridyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups,

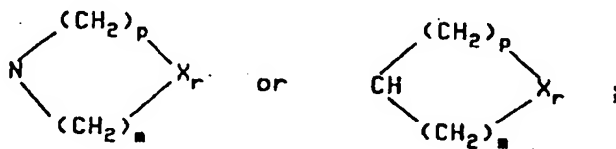
C₃-C₁₂cycloalkyl optionally substituted with one or more halogen, hydroxy, C₁-C₄alkoxy, (C₁-C₄alkyl)SO_x, CONR₇R₈, CO₂R₉, R₁₀, R₁₁, C₃-C₆cycloalkyl optionally substituted with one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups, phenyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, CO₂ or CN groups, or pyridyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups or

may be taken together to form a ring represented by the structure

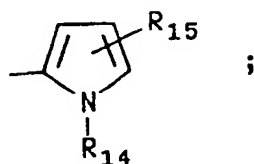


R₇, R₈ and R₉
R₁₀

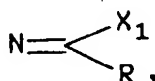
are each independently hydrogen, halogen, CN, NO₂, (C₁-C₄ alkyl)SO_x, (C₁-C₄ haloalkyl)SO_x, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy or C₁-C₆ haloalkoxy; are each independently hydrogen or C₁-C₄ alkyl; is NR₁₂R₁₃,

 R_{11}

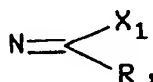
is



R_{12} , R_{13} , R_{14} and R_{15} are each independently hydrogen or C_1 - C_4 alkyl;
 X_1 is chlorine, bromine, or fluorine;
 X is O, S or NR_{14} ;
 r is an integer of 0 or 1;
 p and m are each independently an integer of 0, 1, 2 or 3 with the provisos that only one of p , m or r can be 0 and that the sum of $p + m + r$ must be 4, 5 or 6;
 x is an integer of 0, 1 or 2; or
 the acid addition salts thereof, with the proviso that when Q is

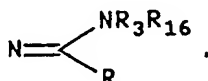


R is C_1 - C_5 alkyl and X_1 is chlorine, then either at least one of A, B or W must be N or R_4 , R_5 , R_6 and Y must be other than hydrogen and n must be 0 and with the further proviso that when Q is



R is phenyl or substituted phenyl and X_1 chlorine, then at least one of A, B or W must be N.

The present invention further provides N-arylamidrazone compounds of formula I wherein A, B, W, Y, n, and R_1 , are as described hereinabove and Q is



with the proviso that when all of A, B and W are other than N, then R and one of R_3 or R_{16} must be other than hydrogen and with the further proviso that when one of A, B or W is N, then Y, R_4 , R_5 or R_6 must be other than C_1 - C_{10} alkyl.

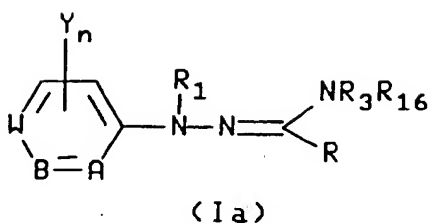
Compositions and methods for the protection of growing plants from attack and infestation by insects and acarina are also provided.

DETAILED DESCRIPTION OF THE INVENTION

A variety of insects and acarina cause great economic loss by damaging or destroying agricultural crops and other valuable plants; by aiding in the spread and development of bacteria, fungi and viruses that produce diseases of plants; and by destroying or lowering the value of stored foods, other products and possessions. Insects and acarina present some of the farmers' greatest problems the world over. The need for alternative and effective insect and acarid control is a global concern.

It has now been found that the substituted N-arylhydrazone derivatives of formula I are especially efficacious insecticidal and acaricidal agents, particularly against Coleoptera, Lepidoptera and Acarina.

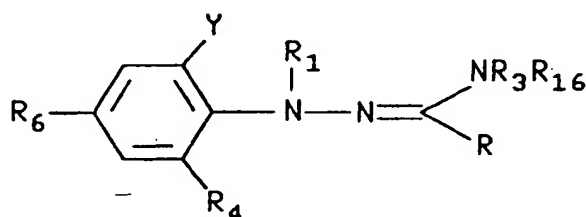
The formula Ia amidrazone compounds of the present invention have the structural formula



wherein A, B, W, Y, n, R, R₁, R₃ and R₁₆ are described hereinabove. The term halogen as used in the specification and claims designates chlorine, fluorine, bromine or iodine. The term acid addition salts designates those salts formed by acids commonly known in the art such as hydrogen chloride, hydrogen bromide, hydrogen bisulfate, hemi-hydrogen sulfate and the like. In the above definition when n is O then Y is hydrogen.

Preferred compounds of the invention are those wherein R, R₃ and R₁₆ are each independently hydrogen or C₁-C₆ alkyl, A is C-R₄, B is C-R₅, W is C-R₆, Y is halogen and n is 1. Particularly preferred compounds are those wherein R₁ is hydrogen, R₄ is halogen, R₅ is hydrogen and/or R₆ is C₁-C₆ alkyl substituted with one or more halogens, preferably trifluoromethyl.

Other preferred compounds of the invention are compounds having the structure



wherein

R is C₁-C₁₀ alkyl;

R₁ is hydrogen or C₁-C₄ alkyl;

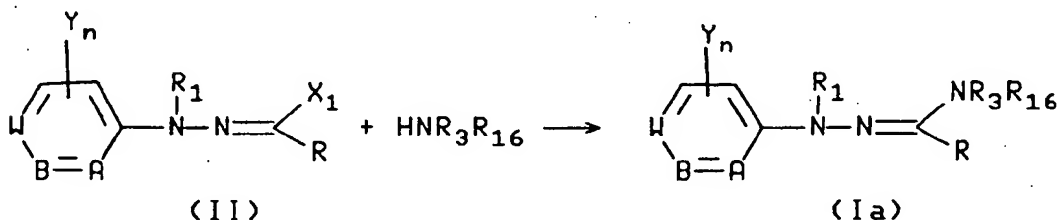
R₃ is C₁-C₁₀ alkyl;

R₁₆ is hydrogen or C₁-C₁₀ alkyl; and

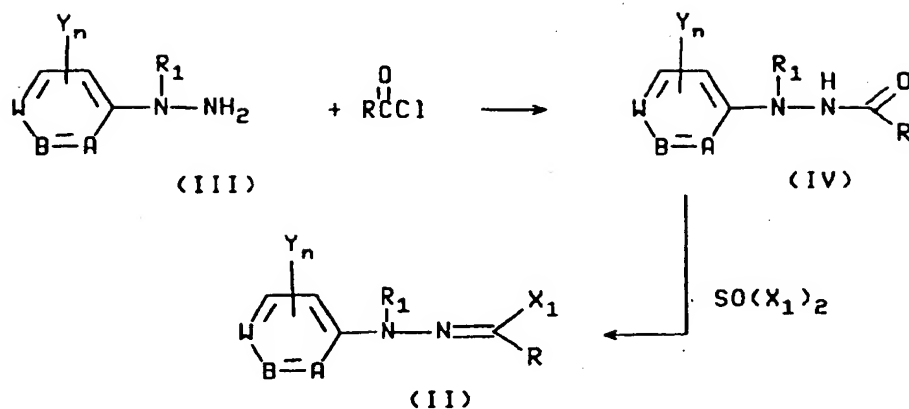
R₄, R₆ and Y are each independently hydrogen, halogen, CN, NO₂, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, or C₁-C₆ haloalkoxy.

The N-arylamidrazones of formula Ia may be prepared by reacting an acid chloride, hydrazone (hydrazinoyl chloride) of formula II with an amine compound, HNR₃R₁₆, as shown in flow diagram I.

Flow Diagram I

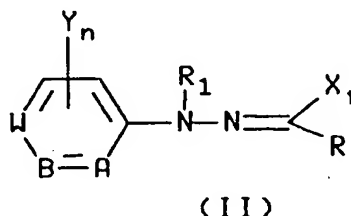


Compounds of formula II may be prepared by reacting a suitable arylhydrazine of formula III with the appropriate acid chloride, RCOCl, to obtain an N-arylhazide of formula IV and reacting the formula IV hydrazide with a halogenating agent such as thionyl halide to give the desired formula II N-arylhazidinoyl halide product. The reaction is illustrated in flow diagram II.

Flow Diagram II

The substituted N-arylhydrazine derivatives of the present invention are effective for controlling insect and acarid pests. Said compounds are also effective for protecting growing or harvested crops from attack and infestation by such pests.

Compounds useful in the inventive method include N-arylhydrazinoyl halide compounds of formula II. The insecticidal and acaricidal formula II hydrazinoyl halides of the present invention have the structural formula



wherein A, B, W, Y, n, R, R₁ and X₁ are described hereinabove.

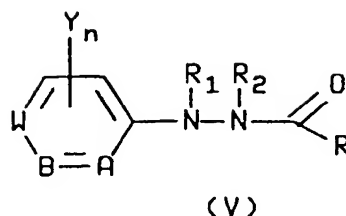
Preferred compounds of formula II are those compounds wherein R₁ is hydrogen, A is C-R₄, B is C-R₅, W is C-R₆, Y is halogen or nitro and n is 1. Particularly preferred are those wherein R₄ is halogen, R₅ is hydrogen and R₆ is C₁-C₆ alkyl substituted with one or more halogens, preferably trifluoromethyl.

Other preferred compounds of formula II are those in which R is optionally substituted C₃-C₁₂ cycloalkyl or C₁-C₁₀ haloalkyl, preferably C₁-C₆ haloalkyl.

Compounds of formula II wherein X₁ is fluorine may be prepared from compounds of formula II wherein X₁ is chlorine or bromine by a halogen exchange reaction using sodium fluoride or hydrogen fluoride such as that described by March in *Advanced Organic Chemistry*, 4 Ed. (1992), p. 438.

Further compounds useful in the method of invention include substituted carboxylic acid, N-arylhydrazide compounds of formula V.

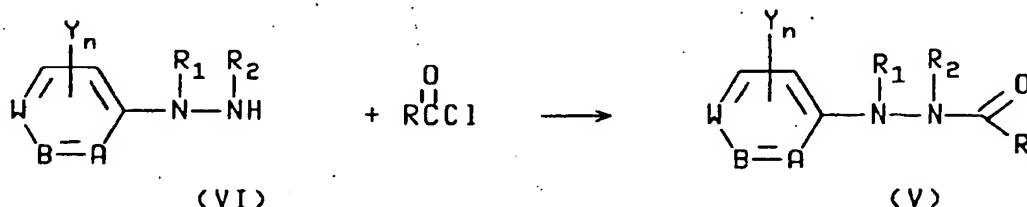
The insecticidal and acaricidal formula V N-arylhydrazides of the present invention have the structural formula



10 Preferred compounds of formula V for use in the method of the invention are those compounds wherein R is hydrogen or C₁-C₆ alkyl, A is C-R₄, B is C-R₅, W is C-R₆, Y is halogen or nitro and n is 1. Particularly preferred formula V N-arylhydrazides are those wherein R₄ is halogen, R₅ is hydrogen and R₆ is C₁-C₆ alkyl substituted with one or more halogens, preferably trifluoromethyl.

15 Compounds of formula V may be prepared by reacting a suitable arylhydrazine of formula VI with the appropriate acid chloride, RCOCl, to yield the desired N-arylhydrazide of formula V. The reaction is illustrated in flow diagram III.

Flow Diagram III



Growing or harvested crops may be protected from attack or infestation by insect or acarid pests by applying to the foliage of the crops, or to the soil or water in which they are growing, a pesticidally effective amount of a formula I N-arylhydrazine derivative.

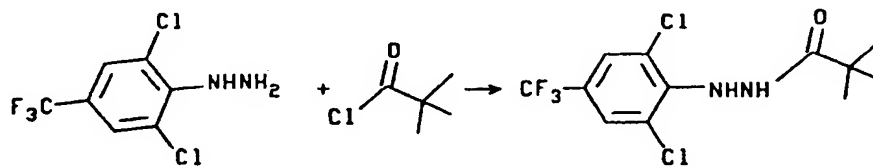
35 In practice, generally about 10 ppm to 10,000 ppm, preferably about 100 to 5,000 ppm of the formula I compound dispersed in a liquid carrier, when applied to the plants or the soil or water in which they are growing, is effective to protect the plants from insect and acarina attack and infestation. Soil application of the formula I compounds is particularly effective for the control of the post-embryonic development stages of Coleoptera and Diptera. Applications, such as spray applications, of compositions of the invention are generally effective at rates which provide about 0.125 kg/ha to about 250 kg/ha, preferably about 10 kg/ha to 100 kg/ha. Of course, it is contemplated that higher or lower rates of application of the N-arylhydrazine derivatives may be used dependent upon the prevailing environmental circumstances such as population density, degree of infestation, stage of plant growth, soil conditions, weather conditions and the like.

45 Advantageously, the formula I compounds may be used in conjunction with, or in combination with other biological and chemical control agents including other insecticides, nematocides, acaricides, molluscicides, fungicides and bactericides such as nuclear polyhedrosis viruses, pyrroles, arylpyrroles, halobenzoylureas, pyrethroids, carbamates, phosphates, and the like.

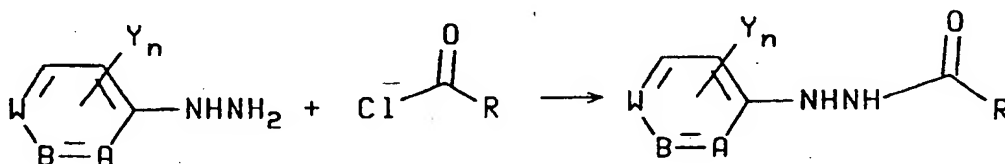
Typical formulations suitable for the formula I N-arylhydrazine derivatives are granular compositions, flowable compositions, wettable powders, dusts, microemulsions, emulsifiable concentrates and the like. All compositions which lend themselves to soil, water and foliage application and provide effective plant protection are suitable. Compositions of the invention include the formula I N-arylhydrazine derivatives admixed with an inert solid or liquid carrier.

55 Where compositions of the invention are to be employed in combination treatments with other biological or chemical agents, the composition may be applied as an admixture of the components or may be applied sequentially.

For a more clear understanding of the invention, specific examples thereof are set forth below. These examples are merely illustrative, and are not to be understood as limiting the scope and underlying principles of the invention in any way.

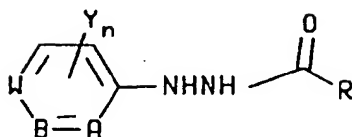
EXAMPLE 1**Preparation of 2,2-Dimethylpropionic acid,2-(2,6-dichloro- α,α,α -trifluoro-p-tolyl)hydrazid**

A solution of 2,6-dichloro-4-(trifluoromethyl)phenylhydrazine (50.0 g, 0.20 mol) in methylene chloride is treated dropwise with trimethylacetyl chloride (30.6 g, 0.254 mol), stirred for 30 minutes, treated with 10% aqueous NaOH and stirred for 3 hours. The phases are separated; the organic phase is washed with water, dried over MgSO₄ and concentrated in vacuo to give an off-white solid residue. The solid is recrystallized from 1,2-dichloroethane to give the title product as a white solid, 55 g (82% yield), mp 140-141°, identified by ¹HNMR, ¹³CNMR and IR spectral analyses.

EXAMPLES 2-42**Preparation of substituted N-arylhydrazide derivatives**

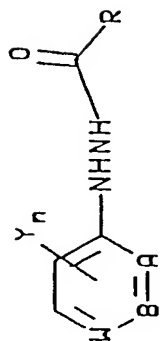
Using essentially the same procedure described above for Example 1 and substituting the appropriate arylhydrazine and acid chloride, the compounds shown in Table I are prepared and identified by ¹HNMR, ¹³CNMR and IR spectral analyses.

TABLE I



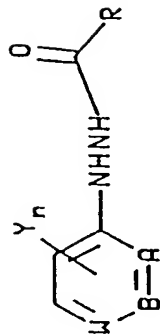
Example Number	A	B	W	Yn	R	mp °C
2	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₂ CHCH ₂	135-136
3	C-Cl	CH	C-Cl	6-Cl	(CH ₃) ₃ C	124-125.5
4	C-Cl	CH	CH	6-Cl	(CH ₃) ₃ C	114-115
5	C-Br	CH	C-CF ₃	6-Br	(CH ₃) ₃ C	118-120
6	C-Br	CH	C-CF ₃	6-Br	CH ₃	173-175
7	C-Br	CH	C-CF ₃	6-Br	C ₆ H ₅	181-184

TABLE I (Continued)



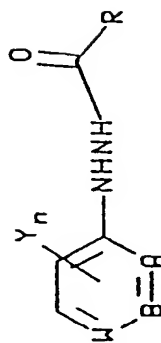
Example Number	A	B	W	Yn	R	mp °C
8	C-CH ₃	CH	C-Cl	H	(CH ₃) ₃ C	103-106
9	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ CCH ₂	125-127
10	C-Cl	CH	C-Cl	6-Cl	pClC ₆ H ₅	188-190
11	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₂ CH	158-159
12	C-Cl	CH	C-Cl	6-Cl	cyclopropyl	186-188
13	C-Cl	CH	C-CF ₃	6-Cl	CH ₃ CH ₂ C(CH ₃) ₂	121-123
14	C-H	CH	C-CF ₃	H	(CH ₃) ₃ C	136-139
15	C-Cl	CH	C-CF ₃	H	(CH ₃) ₃ C	143-145

TABLE I (Continued)



Example Number	A	B	W	Yn	R	mp °C
16	C-Cl	CH	C-CF ₃	6-Cl		125-127
17	C-Cl	C-Cl	C-Cl	5,6-diCl	(CH ₃) ₃ C	
18	N	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	151-151.5
19	C-Cl	CH	C-Cl	6-Cl		138-140
20	C-Cl	CH	C-CF ₃	6-Cl		137-139
21	C-CF ₃	CH	CH	H	(CH ₃) ₃ C	98-100
22	C-Cl	CH	C-CF ₃	6-Cl		101-103
23	C-Cl	CH	C-Cl	6-Cl	cyclohexyl	188-189

TABLE I (Continued)



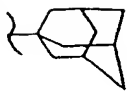
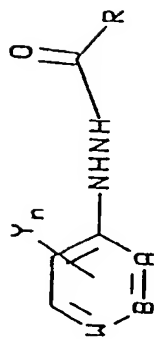
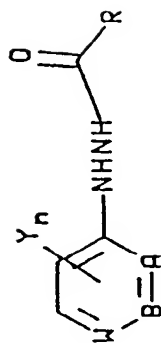
Example Number	A	B	W	Yn	R	mp °C
24	C-Cl	CH	C-CF ₃	6-Cl	C ₆ H ₅ C(CH ₃) ₂	104-105
25	C-Cl	CH	C-Cl	6-Cl	CF ₃ CF ₂	131-132
26	C-Cl	CH	C-Cl	6-Cl	(CH ₃) ₂ CH	164-165
27	C-Cl	CH	C-CF ₃	6-Cl	cyclopropyl	172-174
28	C-Cl	CH	C-Cl	6-Cl	CH ₃ CH ₂ C(CH ₃) ₂	132-134
29	C-Cl	CH	C-CF ₃	6-Cl		160-162
30	C-Br	CH	C-CF ₃	6-Br	(CH ₃) ₃ C	140-141
31	C-Cl	CH	C-Cl	6-Cl	CH ₃ (CH ₂) ₅ C(CH ₃) ₂	

TABLE I (Continued)



Example Number	A N	B N	W C-Cl	Yn H	R (CH ₃) ₃ C	mp °C 178-182
32						
33	C-Cl	CH	C-CF ₃	6-Cl		121-123
34	C-Cl	CH	C-CF ₃	6-Cl	BClC ₆ H ₅ C(CH ₃) ₂	105-107
35	C-Cl	CH	C-CF ₃	6-Cl	ClCH ₂ C(CH ₃) ₂	119-120
36	C-Cl	CH	C-CF ₃	6-Cl		174-175
37	C-Cl	CH	C-Cl	6-Cl	ClCH ₂ C(CH ₃) ₂	124-125
38	C-Cl	CH	CH	5-CF ₃	(CH ₃) ₃ C	170-177.5
39	C-Cl	CH	C-CF ₃	6-Cl	1-methylcyclohexyl	105-107

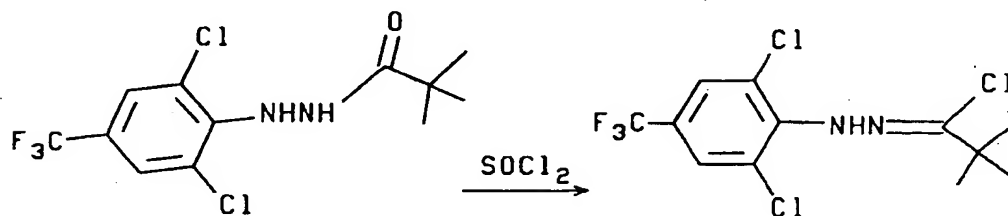
TABLE I (Continued)



Example Number	A	B	W	Yn	R	mp °C
40	CH	C-CF ₃	CH	H	(CH ₃) ₃ C	158-160
41	C-F	C-F	C-F	5,6-diF	(CH ₃) ₃ C	154-157
42	C-Br	CH	F	6-Br	(CH ₃) ₃ C	118-120

EXAMPLE 43

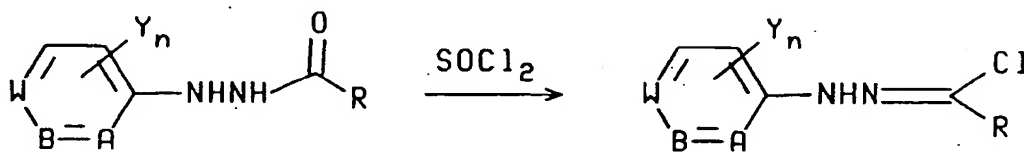
Preparation of 1-chloro-2,2-dimethylpropionaldehyde, 2-(2,6-Dichloro- α,α,α -trifluoro-p-tolyl)hydrazone



A mixture of 2,2-dimethyl-2-(2,6-dichloro- α,α,α -trifluoro-p-tolyl)hydrazide propionic acid (50.0 g, 0.152 mol) and thionyl chloride (53.8 g, 0.452 mol) in toluene is heated at reflux temperature for 8 hours, cooled to room temperature and concentrated in vacuo to give an oil residue. The oil is dissolved in hexanes and passed through a silica gel filtercake. The filtercake is washed with several portions of hexanes. The filtrates are combined and concentrated in vacuo to give the title product as a yellow oil, 47.2 g (90% yield), identified by ^1HMR , $^{13}\text{CNMR}$ and IR spectral analyses.

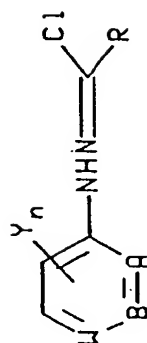
EXAMPLES 44-84

Preparation of substituted N-aryldiazinoyl chlorides



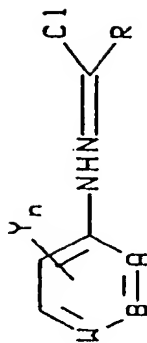
Using essentially the same procedure as described above in Example 43 and substituting the appropriate hydrazide substrate, the compounds shown in Table II are prepared and identified by ^1HMR , $^{13}\text{CNMR}$ and IR spectral analyses.

TABLE II



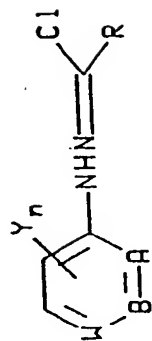
Example Number	A	B	W	Yn	R	mp °C
44	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₂ CHCH ₂	
45	C-Cl	CH	C-Cl	6-Cl	(CH ₃) ₃ C	44.5-45.5
46	C-Cl	CH	CH	6-Cl	(CH ₃) ₃ C	
47	C-Br	CH	C-F	6-Br	(CH ₃) ₃ C	
48	C-Br	CH	C-CF ₃	6-Br	CH ₃	
49	C-Br	CH	C-CF ₃	6-Br	C ₆ H ₅	

TABLE II (Continued)



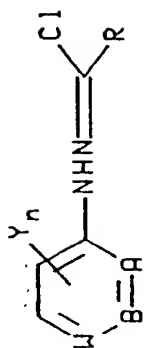
Example Number	A	B	W	Yn	R	mp °C
50	C-CH ₃	CH	C-Cl	H	(CH ₃) ₃ C	
51	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ CCH ₂	
52	C-Cl	CH	C-Cl	6-Cl	EtC ₆ H ₅	120
53	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₂ CH	
54	C-Cl	CH	C-Cl	6-Cl	cyclopropyl	
55	C-Cl	CH	C-CF ₃	6-Cl	CH ₃ CH ₂ C(CH ₃) ₂	
56	C-H	CH	C-CF ₃	H	(CH ₃) ₃ C	

TABLE II (Continued)



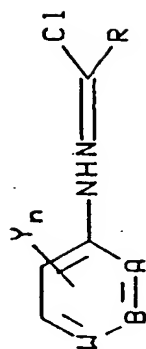
Example Number	A	B	W	Yn	R	mp °C
57	C-Cl	CH	C-CF ₃	H	(CH ₃) ₃ C	
58	C-Cl	CH	C-CF ₃	6-Cl		
59	C-Cl	C-Cl	C-Cl	5,6-diCl	(CH ₃) ₃ C	
60	N	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	
61	C-Cl	CH	C-Cl	6-Cl		
62	C-Cl	CH	C-CF ₃	6-Cl	BClC ₆ H ₅ OC(CH ₃) ₂	
63	C-CF ₃	CH	CH	H	(CH ₃) ₃ C	

TABLE II (Continued)



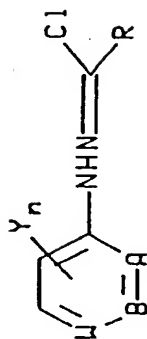
Example Number	A	B	W	Yn	R	mp °C
64	C-Cl	CH	C-CF ₃	6-Cl		
65	C-Cl	C-CH	C-Cl	6-Cl	cyclohexyl	
66	C-Cl	C-CH	C-CF ₃	6-Cl	C ₆ H ₅ C(CH ₃) ₂	
67	C-Cl	CH	C-Cl	6-Cl	CF ₃ CF ₂	
68	C-Cl	CH	C-Cl	6-Cl	(CH ₃) ₂ CH	
69	C-Cl	CH	C-CF ₃	6-Cl	cyclopropyl	
70	C-Cl	CH	C-Cl	6-Cl	CH ₃ CH ₂ C(CH ₃) ₂	

TABLE II (Continued)



Example Number	A	B	W	Yn	R	mp °C 110-111
71	C-Cl	CH	C-CF ₃	6-Cl		
72	C-Br	CH	C-CF ₃	6-Br	(CH ₃) ₃ C	
73	C-Cl	CH	C-Cl	6-Cl	CH ₃ (CH ₂) ₅ C(CH ₃) ₂	
74	N	N	C-Cl	H	(CH ₃) ₃ C	
75	C-Cl	CH	C-CF ₃	6-Cl		
76	C-Cl	CH	C-CF ₃	6-Cl	PhC(CH ₃) ₂ C(CH ₃) ₂	85-88
77	C-Cl	CH	C-CF ₃	6-Cl	ClCH ₂ C(CH ₃) ₂	

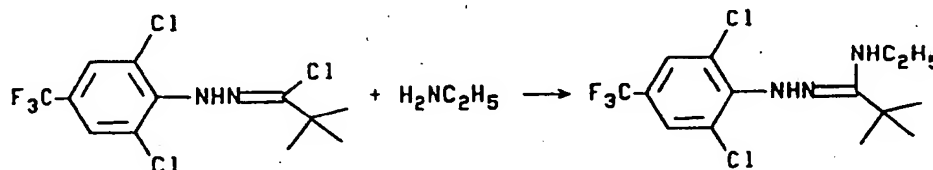
TABLE II (Continued)



Example Number	A	B	W	Yn	R	mp °C 71-73
78	C-Cl	CH	CCF ₃	6-Cl		
79	C-Cl	CH	C-Cl	6-Cl	ClCH ₂ C(CH ₃) ₂	
80	C-Cl	CH	CH	5-CF ₃	(CH ₃) ₃ C	
81	C-Cl	CH	C-CF ₃	6-Cl	1-methylcyclohexyl	
82	CH	C-CF ₃	CH	H	(CH ₃) ₃ C	
83	CH	CH	CH	5-F	(CH ₃) ₃ C	
84	C-Br	CH	F	6-Br	(CH ₃) ₃ C	

EXAMPLE 85

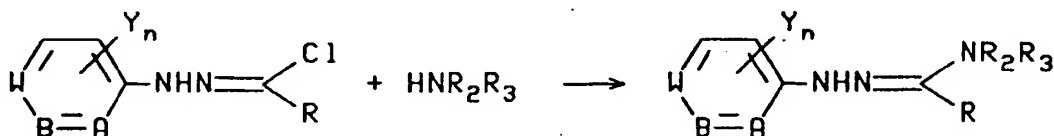
Preparation of N-Ethyl-2,2-dimethylpropionamide, 2-(2,6-Dichloro- α,α,α -trifluoro-p-tolyl)hydrazone



A solution of (2,6-dichloro- α,α,α -trifluoro-p-tolyl)hydrazone 1-chloro-2,2-dimethylpropionaldehyde (20.0 g, 0.0575 mol) in tetrahydrofuran is treated dropwise with 70% aqueous ethylamine (28.0 g, 0.144 mol) at room temperature, stirred for 1 hour and concentrated in vacuo to give a semi-solid residue. The semi-solid is dispersed in ether and water. The phases are separated; the organic phase is washed with water, dried over MgSO_4 and concentrated in vacuo to give the title product as a yellow oil, 19.8 g (97% yield), identified by ^1H NMR, ^{13}C NMR and IR spectral analyses.

EXAMPLES 86-169

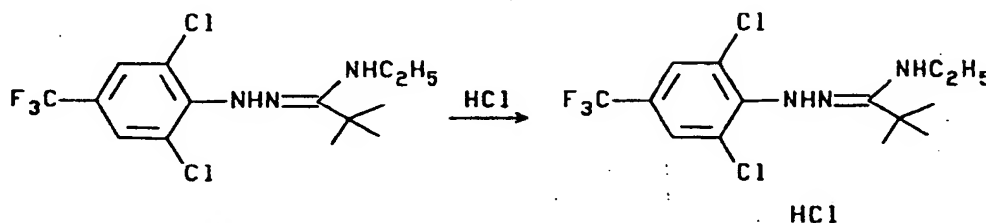
Preparation of substituted N-arylamidrazones



Using essentially the same procedure described above in Example 85 and substituting the appropriate hydrazinoylchloride and a suitable amine, the compounds shown in Table III are prepared and identified by ^1H NMR, ^{13}C NMR and IR spectral analyses.

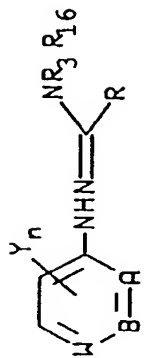
Hydrochloride salts of the invention may be prepared in accordance with the procedure outlined below.

Example 146 - Preparation of N-Ethyl-2,2-dimethylpropionamide, 2-(2,6-dichloro- α,α,α -trifluoro-p-tolyl)hydrazone hydrochloride



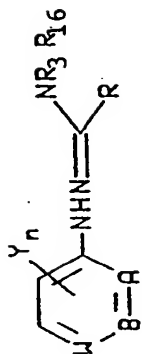
A stirred mixture of N-ethyl-2,2-dimethylpropionamide, 2-(2,6-dichloro- α,α,α -trifluoro-p-tolyl)hydrazone (0.1 g, 2.8 mmol) and hexane is bubbled through with HCl gas for a 30 minute period. The resultant reaction mixture is filtered to give the title compound as a white solid, 1.13 g, mp 202-202.5°C.

TABLE III



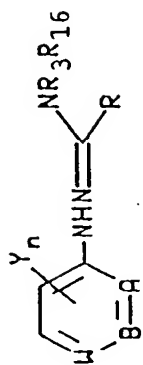
Example Number	A	B	W	Yn	R	R3	R16	mp °C
86	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	PClC ₆ H ₅	H	
87	C-Cl	CH	C-Cl	6-Cl	(CH ₃) ₃ C	CH ₃ CH ₂ CH ₂	H	
88	C-Cl	CH	C-Cl	6-Cl	(CH ₃) ₂ CH	CH ₃ CH ₂ CH ₂	H	48-50
89	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ CCH ₂	CH ₃ CH ₂ CH ₂	H	
90	C-Cl	CH	C-Cl	6-Cl	(CH ₃) ₂ CH	cyclopropyl	H	
91	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ CCH ₂	CH ₃ CH ₂	H	

TABLE III (Continued)



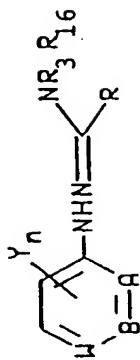
Example Number	A	B	W	Yn	R	R ₃	R ₁₆	mp °C
92	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₂ CH	CH ₃ CH ₂	H	62-64
93	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	CF ₃ CH ₂	H	
94	C-Br	CH	C-CF ₃	6-Br	(CH ₃) ₃ C	CH ₃ CH ₂	H	
95	C-Br	CH	C-CF ₃	6-Br	(CH ₃) ₃ C	CH ₃ CH ₂ CH ₂	H	
96	C-Br	CH	C-CF ₃	6-Br	(CH ₃) ₃ C	C ₆ H ₅ CH ₂	H	
97	C-Br	CH	C-CF ₃	6-Br	(CH ₃) ₃ C	furfuryl	H	

TABLE III (Continued)



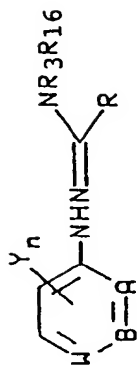
Example Number	A	B	W	Yn	R	R3	R16	mp °C
98	C-Br	CH	C-CF ₃	6-Br	CH ₃	CH ₃ CH ₂	H	
99	C-Br	CH	C-CF ₃	6-Br	C ₆ H ₅	CH ₃ CH ₂	H	
100	C-Cl	CH	C-Cl	6-Cl	(CH ₃) ₃ C	H	H	131-135
101	C-Cl	CH	C-Cl	6-Cl	(CH ₃) ₃ C	CH ₃	CH ₃	61-63
102	C-Cl	CH	C-Cl	6-Cl	(CH ₃) ₃ C	CH ₃ CH ₂	H	
103	C-Cl	CH	C-CF ₃	H	(CH ₃) ₃ C	CH ₃ CH ₂ CH ₂	H	
104	C-Cl	CH	CH	6-Cl	(CH ₃) ₃ C	CH ₃ CH ₂ CH ₂	H	
105	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	H	H	100-102.5

TABLE III (Continued)



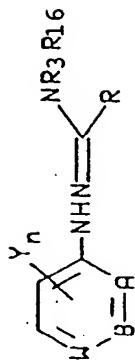
Example Number	A	B	W	Yn	R	R3	R16	mp °C
106	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	CH ₃	H	78-79.5
107	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	CH ₃	CH ₃	
108	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	CH ₃ CH ₂ CH ₂	H	
109	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	(CH ₃) ₃ C	H	67.5-68.5
110	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	(CH ₃) ₂ CHCH ₂	H	
111	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	-CH ₂ CH ₂ CH ₂ CH ₂ -		
112	C-Cl	CH	C-Cl	6-Cl	cyclopropyl	CH ₃ CH ₂	H	65-67

TABLE III (Continued)



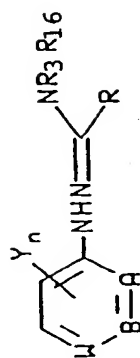
Example Number	A	B	W	Yn	R	R3	R16	mp °C
113	C-Cl	CH	C-CF ₃	6-Cl	CH ₃ CH ₂ C(CH ₃) ₂	CH ₃ CH ₂	H	
114	C-Br	CH	C-CF ₃	6-Br	(CH ₃) ₃ C	(CH ₃) ₂ CH	H	
115	C-Cl	CH	C-CF ₃	H	(CH ₃) ₃ C	-CH ₂ CH ₂ CH ₂ CH ₂ -		
116	C-Cl	CH	C-CF ₃	6-Cl	CH ₃ CH ₂ C(CH ₃) ₂	CH ₃ CH ₂	CH ₃ CH ₂	
117	C-Cl	CH	C-CF ₃	H	(CH ₃) ₃ C	CH ₃ CH ₂	H	
118	C-Cl	CH	C-Cl	6-Cl	CH ₃ CH ₂ C(CH ₃) ₂	CH ₃ CH ₂	H	

TABLE III (Continued)



Example Number	A	B	W	Yn	R	R3	R16	mp °C
119	C-Cl	CH	C-CF ₃	6-Cl	C ₆ H ₅ C(CH ₃) ₂	CH ₃ CH ₂	H	
120	C-Cl	CH	C-CF ₃	H	(CH ₃) ₃ C	-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ -		
121	CH	CH	C-CF ₃	H	(CH ₃) ₃ C	CH ₃ CH ₂	H	
122	CH	CH	C-CF ₃	6-Cl	(CH ₃) ₂ CHCH ₂	CH ₃ CH ₂	H	86.5-88.5
123	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ -		
124	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	cyclohexyl	H	
125	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	C ₆ H ₅ CH ₂ CH ₂	H	

TABLE III (Continued)



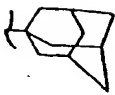
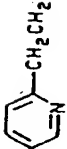
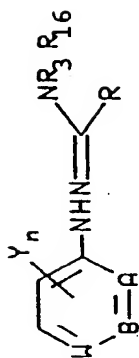
Example Number	A	B	W	Yn	R	R3	R16	mp °C
126	C-Br	CH	C-F	6-Br	(CH ₃) ₃ C	CH ₃ CH ₂	H	
127	C-Cl	C-Cl	C-Cl	5,6-diCl	(CH ₃) ₃ C	CH ₃ CH ₂	H	63-65
128	C-Cl	CH	C-Cl	6-Cl	CH ₃ (CH ₂) ₅ C(CH ₃) ₂	CH ₃ CH ₂	H	
129	C-Cl	CH	C-CF ₃	6-Cl		CH ₃ CH ₂	H	
130	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	CH ₃ (CH ₂) ₂ CH ₂	H	
131	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	(CH ₃) ₂ CH	H	
132	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C		H	

TABLE III (Continued)




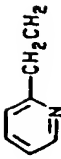
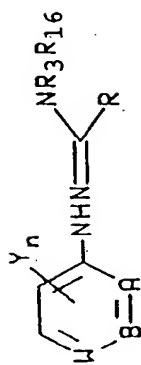
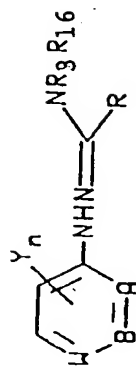
Example Number	A	B	W	Yn	R	R3	R16	mp °C
133	C-Cl	CH	C-Cl	6-Cl	pClC ₆ H ₅	(CH ₃) ₂ CH	H	124-127
134	C-Cl	CH	C-Cl	6-Cl	pClC ₆ H ₅	CH ₃ CH ₂	H	127-132
135	C-Cl	CH	C-CF ₃	6-Cl	C ₆ H ₅ C(CH ₃) ₂	C ₆ H ₅ CH ₂ CH ₂	H	
136	C-Cl	CH	C-CF ₃	6-Cl		CH ₃ CH ₂	H	74-75
137	C-CF ₃	CH	CH	H	(CH ₃) ₃ C	CH ₃ CH ₂	H	
138	C-Cl	CH	C-CF ₃	H	(CH ₃) ₃ C	C ₆ H ₅ CH ₂ CH ₂	H	
139	C-Cl	CH	C-CF ₃	H	(CH ₃) ₃ C		H	

TABLE III (Continued)



Example Number	A	B	W	Yn	R	R ₃	R ₁₆	mp °C
140	CH	CH	C-CF ₃	H	(CH ₃) ₃ C		H	
141	C-Cl	CH	C-CF ₃	6-Cl	pClC ₆ H ₅ C(CH ₃) ₂	CH ₃ CH ₂	H	
142	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	C ₆ H ₅ CH(CH ₃)	H	
143	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	(CH ₃) ₂ NCH ₂ CH ₂	H	
144	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	CH ₃ CH ₂ C(CH ₃) ₂	H	
145	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C		H	100.5-101.5

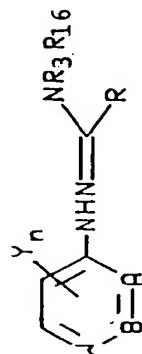
TABLE III (Continued)



Example Number	A	B	W	Yn	R	R3	R16	mp °C
146*	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	CH ₃ CH ₂	H	202-202.5
147	C-Br	CH	C-CF ₃	6-Br	(CH ₃) ₃ C		H	
148	C-Cl	CH	C-CF ₃	6-Cl		CH ₃ CH ₂	H	
149	C-Cl	CH	C-CF ₃	6-Cl		CH ₃ CH ₂	H	
150	C-Cl	CH	C-CF ₃	6-Cl	CH ₃ CH ₂ C(CH ₃) ₂	C ₆ H ₅ CH ₂ CH ₂	H	
151	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	C ₆ H ₅ CH ₂	H	

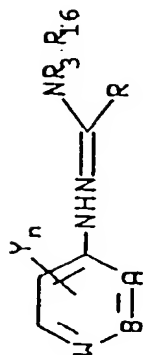
* Hydrochloride salt

TABLE III (Continued)



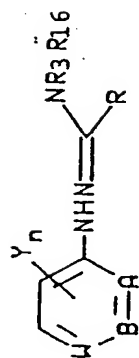
Example Number	A	B	W	Yn	R	R3	R16	mp °C
152	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	CH ₃ CH ₂	CH ₃ CH ₂	
153	C-Cl	CH	C-CF ₃	6-Cl		CH ₃ CH ₂	H	
154	C-Cl	CH	C-CF ₃	6-Cl		(CH ₃) ₂ CH	H	
155	C-Cl	CH	C-CF ₃	6-Cl	ClCH ₂ C(CH ₃) ₂	OCF ₃ CH ₃	H	203-205
156	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	neopentyl	H	
157	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	H ₂ NCOCCH(CH ₃) ₂	H	160-162
158	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C		H	
159	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	ClC ₆ H ₅ -CH ₂ CH ₂	H	

TABLE III (Continued)

Example
Number

A	B	W	Yn	R	R3	R16	mp °C
160	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	H	
161	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	H	
162	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	H	
163	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	H	
164	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C	H	
165	C-Cl	CH	C-CF ₃	6-Cl	1-methylcyclohexyl	H	
166	C-Cl	CH	CH	5-CF ₃	(CH ₃) ₃ C	H	

TABLE III (Continued)



Example Number	A	B	W	Yn	R	R3	R16	mp °C
167	C-F	C-F	C-F	5,6-diF	(CH ₃) ₃ C	CH ₃ CH ₂	H	
168	C-Br	CH	C-F	6-Br	(CH ₃) ₃ C	CH ₃ CH ₂	H	
169	C-Cl	CH	C-CF ₃	6-Cl	(CH ₃) ₃ C		H	

EXAMPLE 170**Insecticidal and Acaricidal Evaluation of N-arylhydrazine Derivatives**

Test solutions are prepared by dissolving the test compound in a 35% acetone in water mixture to give a concentration of 10,000 ppm. Subsequent dilutions are made with water as needed.

Spodoptera eridania, 3rd instar larvae, southern
armyworm

A Sieva limabean leaf expanded to 7-8 cm in length is dipped in the test solution with agitation for 3 seconds and allowed to dry in a hood. The leaf is then placed in a 100 x 10 mm petri dish containing a damp filterpaper on the bottom and ten 3rd instar caterpillars. At 3 and 5 days, observations are made of mortality, reduced feeding, or any interference with normal molting.

Tetranychus urticae(OP-resistant strain), 2-spotted spider mite

Sieva limabean plants with primary leaves expanded to 7-8 cm are selected and cut back to one plant per pot. A small piece is cut from an infested leaf taken from the main colony and placed on each leaf of the test plants. This is done about 2 hours before treatment to allow the mites to move over to the test plant to lay eggs. The size of the cut, infested leaf is varied to obtain about 100 mites per leaf. At the time of test treatment, the piece of leaf used to transfer the mites is removed and discarded. The newly mite-infested plants are dipped in the test solution for 3 seconds with agitation and set in the hood to dry. After 2 days, one leaf is removed and mortality counts are made. After 5 days, another leaf is removed and observations are made of mortality of the eggs and/or newly emerged nymphs.

Diabrotica undecimpunctata howardi, 3rd instar southern
corn rootworm

One cc of fine talc is placed in a 30 ml wide-mouth screw-top glass jar. One mL of the appropriate acetone test solution is pipetted onto the talc so as to provide 1.25 mg of active ingredient per jar. The jars are set under a gentle air flow until the acetone is evaporated. The dried talc is loosened, 1 cc of millet seed is added to serve as food for the insects and 25 mL of moist soil is added to each jar. The jar is capped and the contents thoroughly mixed on a Vortex Mixer. Following this, ten 3rd instar rootworms are added to each jar and the jars are loosely capped to allow air exchange for the larvae. The treatments are held for 6 days when mortality counts are made. Missing larvae are presumed dead, since they decompose rapidly and can not be found. The concentrations used in this test correspond approximately to 50 kg/ha.

The tests are rated according to the scale shown below and the data obtained are shown in Tables IV, V and VI.

RATING SCALE			
Rate	% Mortality	Rate	% Mortality
0	no effect	5	56-65
1	10-25	6	66-75
2	26-35	7	76-85
3	36-45	8	86-99
4	46-55	9	100

TABLE IV
Insecticidal and Acaricidal Evaluation
of N-Arylamidrazones

5

	Compound (Ex. No.)	% Mortality		
		Armyworm ¹ (300 ppm)	2-Spotted Mite ² (300 ppm)	Corn Rootworm ³ (50 kg/ha)
10	85	0	0	100
	86	100	0	80
15	87	40	90	100
	88	---	---	---
20	89	0	0	100
	90	0	0	20
	91	0	80	100
25	92	0	0	100
	93	0	0	100
	94	---	80	100
30	95	80	0	100
	96	100	40	80
35	97	0	0	100
	98	40	0	40
	100	0	40	0
40	101	0	0	60
	102	0	60	100
45	103	40	0	100
	104	0	90	50
	105	20	0	90
50	106	40	0	100

55

TABLE IV (Continued)

	Compound (Ex. No.)	% Mortality		
		Armyworm ¹ (300 ppm)	2-Spotted Mite ² (300 ppm)	Corn Rootworm ³ (50 kg/ha)
5	107	---	---	100
10	108	90	50	100
	109	0	0	50
15	110	0	0	100
	111	100	40	90
20	112	40	100	20
	113	20	100	100
	114	40	100	100
25	115	0	0	100
	116	20	50	100
30	117	20	0	100
	118	50	70	100
	119	100	50	90
35	120	---	30	20
	121	80	40	100
40	122	0	0	40
	123	0	0	60
	124	50	80	100
45	125	0	30	100
	126	0	80	90
50	128	0	0	30
	129	100	40	0

55

TABLE IV (Continued)

	Compound (Ex. No.)	% Mortality		
		Armyworm ¹ (300 ppm)	2-Spotted Mite ² (300 ppm)	Corn Rootworm ³ (50 kg/ha)
5	130	80	80	100
10	131	70	0	100
	132	--	40	100
	133	--	0	0
15	134	0	30	0
	135	0	0	0
20	136	0	70	100
	137	0	0	100
	138	0	0	100
25	139	0	70	100
	140	0	0	50
30	141	100	0	0
	142	0	0	100
	143	0	0	100
35	144	0	0	100
	145	0	0	100
40	146	0	0	100
	147	0	0	100
	148	50	0	100
45	149	100	80	80
	150	0	60	100
50	152	80	0	100

55

TABLE IV (Continued)

5

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15

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25

30

35

Compound (Ex. No.)	% Mortality		
	Armyworm ¹ (300 ppm)	2-Spotted Mite ² (300 ppm)	Corn Rootworm ³ (50 kg/ha)
153	100	0	100
156	---	0	100
157	0	0	100
158	40	0	100
159	0	0	100
160	0	0	100
161	0	0	---
162	0	100	100
163	0	0	100
164	0	0	100
167	0	0	100
168	0	80	90
169	0	0	100

¹Armyworm is 3rd instar larvae, southern armyworm

²2-Spotted Mite is 2-spotted spider mite (OP-resistant)

³Corn Rootworm is 3rd instar southern corn rootworm

45

50

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TABLE VInsecticidal and Acaricidal Evaluationof N-Arylhydrazides

5

Compound (Ex. No.)	Armyworm ¹ (300 ppm)	2-Spotted Mite ² (300 ppm)	Corn Rootworm ³ (50 kg/ha)
-----------------------	------------------------------------	--	--

10

1	8	0	9
---	---	---	---

2	0	0	7
---	---	---	---

15

3	---	---	9
---	-----	-----	---

4	0	0	7
---	---	---	---

5	0	0	8
---	---	---	---

20

6	0	0	0
---	---	---	---

7	0	0	0
---	---	---	---

25

8	5	0	8
---	---	---	---

9	0	0	0
---	---	---	---

10	1	9	3
----	---	---	---

30

11	1	0	9
----	---	---	---

12	4	0	4
----	---	---	---

13	0	9	3
----	---	---	---

35

14	7	0	7
----	---	---	---

15	9	0	3
----	---	---	---

40

16	0	0	0
----	---	---	---

17	1	3	0
----	---	---	---

18	2	0	6
----	---	---	---

45

19	9	0	0
----	---	---	---

20	0	0	0
----	---	---	---

50

21	0	0	7
----	---	---	---

22	0	0	0
----	---	---	---

55

TABLE V(Continued)

5	Compound (Ex. No.)	% Mortality		
		Armyworm ¹ (300 ppm)	2-Spotted Mite ² (300 ppm)	Corn Rootworm ³ (50 kg/ha)
	23	0	0	0
10	24	0	0	0
	25	9	0	8
	26	0	0	0
15	27	4	0	6
	28	2	0	0
20	29	3	0	0
	30	0	2	4
	31	0	0	0
25	32	1	0	0
	33	0	0	0
	34	8	0	2
30	35	5	0	0
	36	8	0	0
35	37	4	0	0
	39	0	0	0
	40	9	0	9
40	41	3	0	9
	42	0	2	4

¹Armyworm is 3rd instar larvae, southern armyworm

²2-Spotted Mite is 2-spotted spider mite (OP-resistant)

³Corn Rootworm is 3rd instar southern corn rootworm

TABLE VI

5	Insecticidal and Acaricidal Evaluation of Substituted N-Arylhydrazinoyl Halides			
	Compound (Ex. No.)	% Mortality		
		Armyworm ¹ (300 ppm)	2-Spotted Mite ² (300 ppm)	Corn Rootworm ³ (50 kg/ha)
	78	90	90	0
	54	80	100	0
10	58	0	0	0
	59	0	100	0
	64	---	90	100
	66	80	100	20
	71	90	90	30
15	73	50	100	0
	77	100	90	80
	79	100	100	100

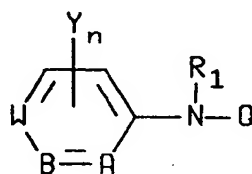
¹Armyworm is 3rd instar larvae, southern armyworm

²2-Spotted Mite is 2-spotted spider mite (OP-resistant)

³Corn Rootworm is 3rd instar southern corn rootworm

Claims

1. A method for the control of insect or acarid pests which comprises contacting said pests or their food supply, habitat or breeding grounds with a pesticidally effective amount of a compound having the structure



(I)

wherein

A

is C-R₄ or N;

B

is C-R₅ or N;

W

is C-R₆ or N with the proviso that at least one of A, B or W must be other than N;

Y

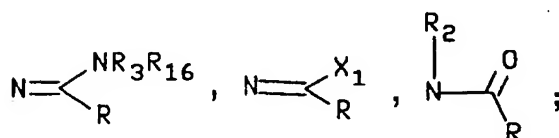
is halogen, CN, NO₂, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy or C₁-C₆ haloalkoxy;

n

is an integer of 0, 1 or 2;

Q

is



R

is hydrogen,

C₁-C₁₀alkyl optionally substituted with one or more halogens, C₃-C₆ cycloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, (C₁-C₄alkyl)SO_x, (C₁-C₄haloalkyl)SO_x, phenyl optionally substituted with one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, (C₁-C₄alkyl)SO_x, (C₁-C₄haloalkyl)SO_x, NO₂ or CN groups, or

phenoxy optionally substituted with one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, (C₁-C₄alkyl)SO_x, (C₁-C₄haloalkyl)SO_x, NO₂ or CN groups,

C₃-C₁₂ cycloalkyl optionally substituted with one or more halogens, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, (C₁-C₄alkyl)SO_x, (C₁-C₄haloalkyl)SO_x,

phenyl optionally substituted with one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups, or

phenoxy optionally substituted with one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups, or

phenyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups;

R₁ and R₂
R₃ and R₁₆

are each independently hydrogen or C₁-C₄alkyl;
are each independently hydrogen,

C₁-C₁₀alkyl optionally substituted with one or more halogen, hydroxy, C₁-C₄alkoxy, (C₁-C₄alkyl)SO_x, CONR₇R₈, CO₂R₉, R₁₀, R₁₁,

C₃-C₆cycloalkyl optionally substituted with one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups,

phenyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, CO₂ or CN groups, or

pyridyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups,

C₃-C₁₀alkenyl optionally substituted with one or more halogen, hydroxy, C₁-C₄alkoxy, (C₁-C₄alkyl)SO_x, CONR₇R₈, CO₂R₉, R₁₀, R₁₁,

C₃-C₆cycloalkyl optionally substituted with one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups,

phenyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, CO₂ or CN groups, or

pyridyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups,

C₃-C₁₀alkynyl optionally substituted with one or more halogen, hydroxy, C₁-C₄alkoxy, (C₁-C₄alkyl)SO_x, CONR₇R₈, CO₂R₉, R₁₀, R₁₁,

C₃-C₆cycloalkyl optionally substituted with one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups,

phenyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, CO₂ or CN groups, or

pyridyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups,

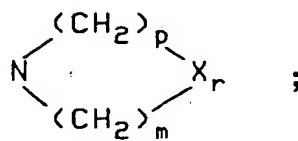
C₃-C₁₂cycloalkyl optionally substituted with one or more halogen, hydroxy, C₁-C₄alkoxy, (C₁-C₄alkyl)SO_x, CONR₇R₈, CO₂R₉, R₁₀, R₁₁,

C₃-C₆cycloalkyl optionally substituted with one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups,

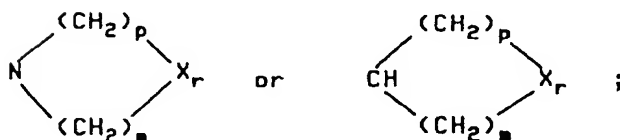
phenyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, CO₂ or CN groups, or

pyridyl optionally substituted with one or more halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, NO₂ or CN groups or

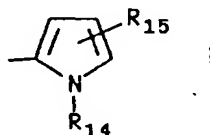
may be taken together to form a ring represented by the structure



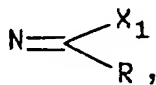
R_4, R_5 and R_6 are each independently hydrogen, halogen, CN, NO_2 , $(\text{C}_1\text{-C}_4\text{alkyl})\text{-SO}_x$, $(\text{C}_1\text{-C}_4\text{haloalkyl})\text{SO}_x$, $\text{C}_1\text{-C}_6\text{alkyl}$, $\text{C}_1\text{-C}_6\text{haloalkyl}$, $\text{C}_1\text{-C}_6\text{alkoxy}$ or $\text{C}_1\text{-C}_6\text{haloalkoxy}$;
 R_7, R_8 and R_9 are each independently hydrogen or $\text{C}_1\text{-C}_4\text{alkyl}$;
 R_{10} is $\text{NR}_{12}\text{R}_{13}$;



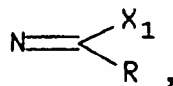
R_{11} is



R_{12}, R_{13}, R_{14} and R_{15} are each independently hydrogen or $\text{C}_1\text{-C}_4\text{alkyl}$;
 X is O, S or NR_{14} ;
 X_1 is chlorine, bromine or fluorine;
 r is an integer of 0 or 1;
 p and m are each independently an integer of 0, 1, 2 or 3 with the proviso that only one of p, m or r can be 0 and with the further proviso that the sum of $p + m + r$ must be 4, 5 or 6;
 x is an integer of 0, 1 or 2; or
the acid addition salts thereof with the proviso that when Q is

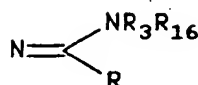


R is $\text{C}_1\text{-C}_5\text{alkyl}$ and X_1 is chlorine, then either at least one of A, B or W must be N or R_4, R_5, R_6 and Y must be other than hydrogen and n must be 0 and with the further proviso that when Q is



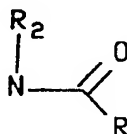
R is phenyl or substituted phenyl and X_1 is chlorine, then at least one of A, B or W must be N.

2. The method according to claim 1 wherein
Q is



3. The method according to claim 2 wherein A is C-R₄, B is CH, W is C-R₆, Y is halogen, n is 1, R₁ is hydrogen, R₄ and R₆ are each independently halogen or C₁-C₆alkyl substituted with one or more halogens, and R, R₃ and R₁₆ are each independently hydrogen or C₁-C₁₀alkyl.

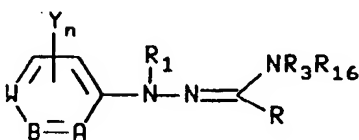
4. The method according to claim 1 wherein Q is



5. The method according to claim 4 wherein R₁ and R₂ are hydrogen, R is C₁-C₆alkyl, A is C-R₃, B is C-R₄, W is C-R₅, Y is halogen, n is 1, R₃ is halogen, R₄ is hydrogen and R₅ is C₁-C₆alkyl substituted with one or more halogens.

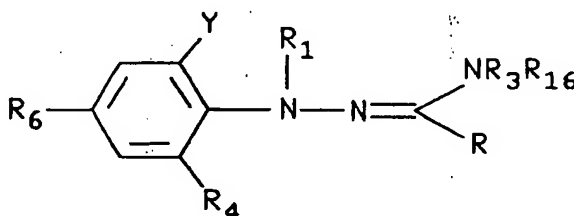
6. The method according to claim 5 wherein the compound is 2,2-dimethylpropionic acid, 2-(2,6-dichloro- α,α,α -trifluoro-p-tolyl)hydrazide.

7. A compound having the structure



wherein A, B, W, Y, n, R, R₁, R₃ and R₁₆ are described in claim 1 with the proviso that when all of A, B and W are other than N, then R and one of R₃ or R₁₆ are other than hydrogen and with the further proviso that when one of A, B or W is N, then Y, R₄, R₅ or R₆ must be other than C₁-C₁₀alkyl.

8. The compound according to claim 7 having the structure



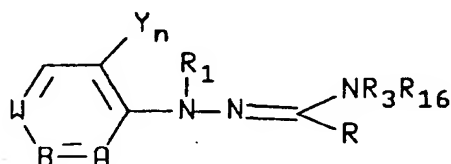
wherein

- | | |
|---------------------------------------|---|
| R | is C ₁ -C ₁₀ alkyl; |
| R ₁ | is hydrogen or C ₁ -C ₄ alkyl; |
| R ₃ | is C ₁ -C ₁₀ alkyl; |
| R ₁₆ | is hydrogen or C ₁ -C ₁₀ alkyl; and |
| R ₄ , R ₆ and Y | are each independently hydrogen, halogen, CN, NO ₂ , C ₁ -C ₆ alkyl, C ₁ -C ₆ haloalkyl, |

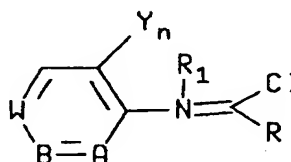
C₁-C₆ alkoxy or C₁-C₆ haloalkoxy.

9. The compound according to claim 8 N-ethyl-2,2-dimethylpropionamide, 2-(2,6-dichloro- α,α,α -trifluoro-p-tolyl)hydrazone

10. A process for the preparation of a compound having the structure

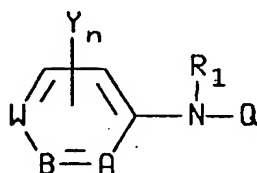


wherein A, B, W, Y, n, R, R₁, R₃ and R₁₆ are described in claim 1 which comprises reacting a compound having the structure



with at least one molar equivalent of an amine compound, HNR₃R₁₆.

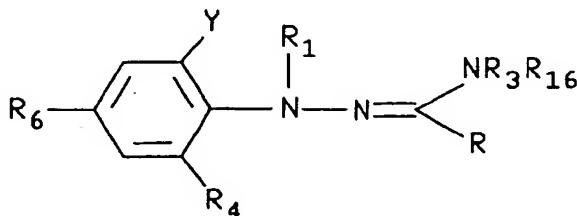
11. A composition for controlling insect or acarid pests which comprises an inert liquid or solid carrier and a pesticidally effective amount of a compound of formula I



(I)

wherein A, B, W, Y, n, R₁ and Q are described in claim 1.

12. The composition according to claim 11 wherein the formula I compound has the structure



and
R
R₁

is C₁-C₁₀ alkyl;
is hydrogen or C₁-C₄ alkyl;

R₃ is C₁-C₁₀alkyl;
R₁₆ is hydrogen or C₁-C₁₀alkyl; and
R₄, R₆ and Y are each independently hydrogen, halogen, CN, NO₂, C₁-C₆alkyl, C₁-C₆ haloalkyl,
C₁-C₆alkoxy or C₁-C₆ haloalkoxy.

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EUROPEAN SEARCH REPORT

Application Number
EP 93 11 9754

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	GB-A-736 473 (BATAAFSCHE PETROLEUM) * claim 1 * ---	1-3, 11, 12	A01N37/28 A01N37/52 A01N43/40 A01N43/58 C07C257/22
X	EP-A-0 325 983 (HOECHST) * claims * ---	1, 4, 11	
X	US-A-3 745 215 (G. KAUGARS) * column 1, line 30 - line 55 * ---	1, 11	
X	US-A-3 917 849 (R. BOESCH) * claims * ---	1, 11	
X	US-A-3 935 315 (R. BOESCH) * claims * ---	1, 11	
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X	US-A-3 214 334 (H.E. FREUND ET AL.) * column 1, line 11 - line 27 * ---	11	A01N C07C
X	FR-A-2 184 974 (BAYER) * claims * ---	11	
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X	US-A-3 505 403 (H.G. VIEHE) * claim 6 * ---	7, 8	
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15 April 1994	Examiner Decorte, D
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons a : member of the same patent family, corresponding document			



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X	JOURNAL OF THE CHEMICAL SOCIETY, PERKIN TRANSACTIONS 2 1986, LETCHWORTH GB pages 537 - 541 I.D.CUNNINGHAM ET AL. 'Acid, base, and uncatalysed isomerisation of z- to e- amidine' *page 537, formula 2*	7,8,10	
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Place of search THE HAGUE		Date of completion of the search 15 April 1994	Examiner Decorte, D
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